Chemical Sensors: an Overview

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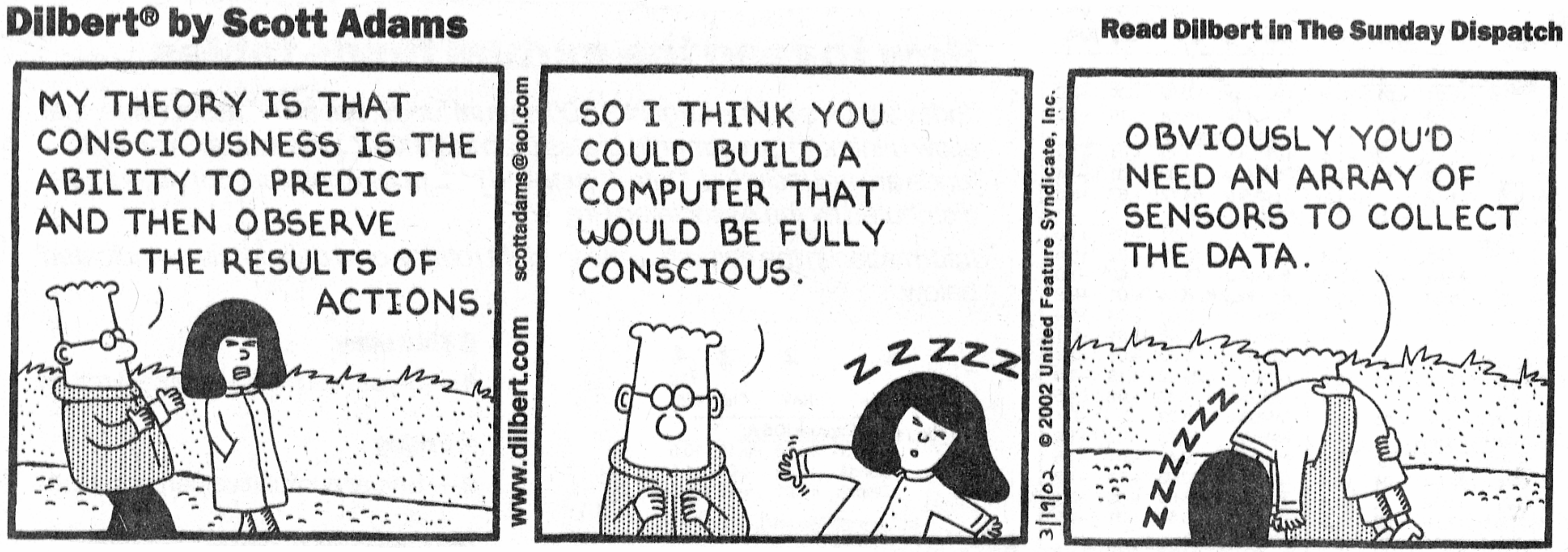
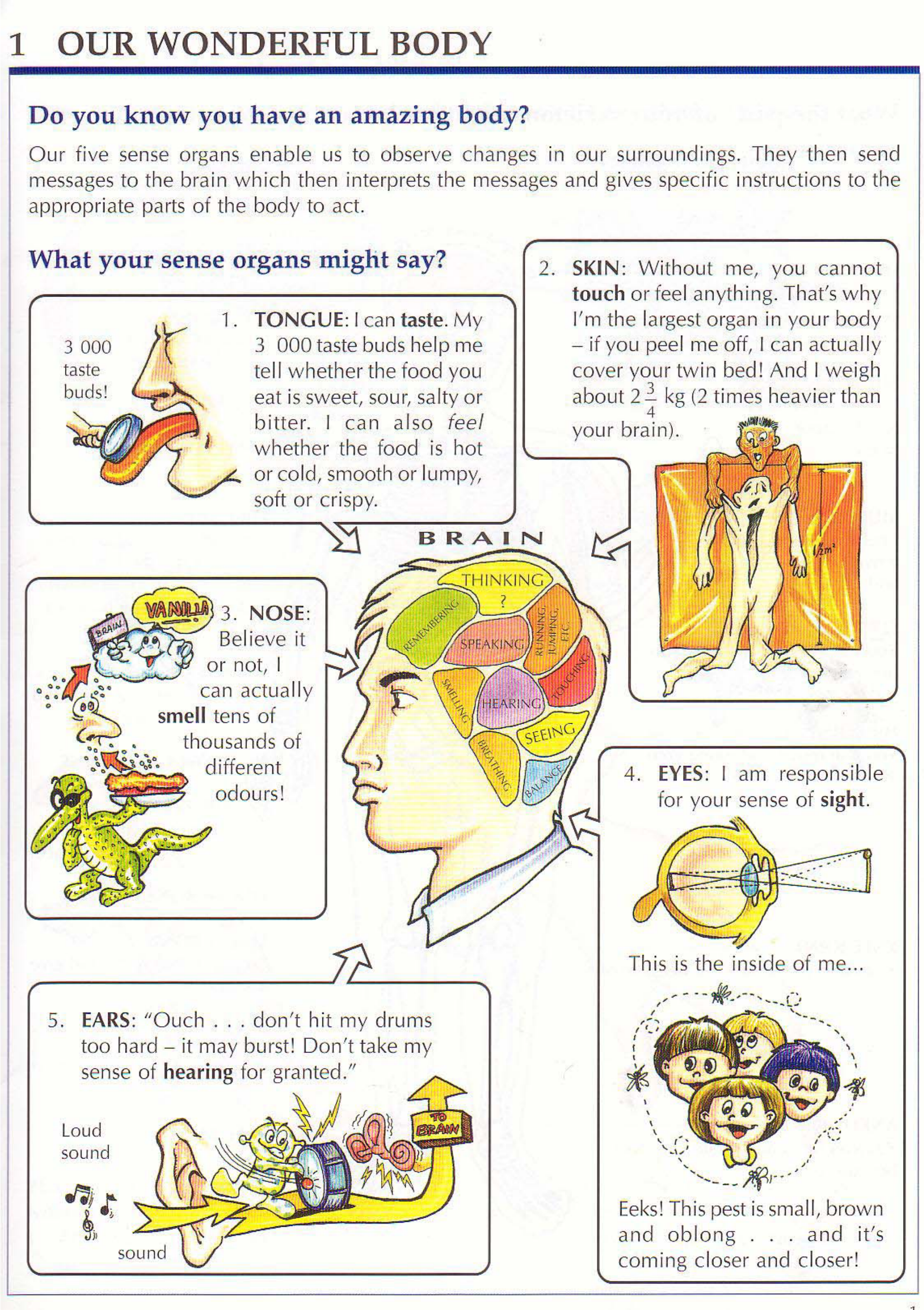
CISM
Center for Industrial
Sensors and Measurements
A National Science Foundation Center

Sensor is even on Dilbert's mind!



Sensors in our body



1 OUR WONDERFUL BODY

Do you know you have an amazing body?

Our five sense organs enable us to observe changes in our surroundings. They then send messages to the brain which then interprets the messages and gives specific instructions to the appropriate parts of the body to act.

What your sense organs might say?

1. **TONGUE:** I can **taste**. My 3 000 taste buds help me tell whether the food you eat is sweet, sour, salty or bitter. I can also *feel* whether the food is hot or cold, smooth or lumpy, soft or crispy.

2. **SKIN:** Without me, you cannot **touch** or feel anything. That's why I'm the largest organ in your body – if you peel me off, I can actually cover your twin bed! And I weigh about $2\frac{3}{4}$ kg (2 times heavier than your brain).

3. **NOSE:** Believe it or not, I can actually **smell** tens of thousands of different odours!

4. **EYES:** I am responsible for your sense of **sight**.

This is the inside of me...

Eeks! This pest is small, brown and oblong . . . and it's coming closer and closer!

5. **EARS:** "Ouch . . . don't hit my drums too hard – it may burst! Don't take my sense of **hearing** for granted."

On-going work on

√ Electronic nose

√ Electronic tongue

Sensor Types

- Grouping based on the form of energy in which signals are received
- Signal domains with examples

Mechanical	**Length, Area, volume, all time derivatives such as linear/angular velocity/acceleration, mass flow, force, torque, pressure, acoustic wavelength and intensity**
Thermal	**Temperature, (specific) heat, entropy, heat flow, state of matter**
Electrical	**Voltage, current, charge, resistance, inductance, capacitance, dielectric constant, polarization, electric field, frequency, dipole moment**
Magnetic	**Field intensity, flux density, magnetic moment, permeability**
Radiant	**Intensity, phase, wavelength, polarization, reflectance, transmittance, refractive index**
Chemical	**Composition, concentration, reaction rate, pH, oxidation/reduction potential**

Physical and Chemical Transduction Principles

Secondary Signal Primary Signal	Mechanical	Thermal	Electrical	Magnetic	Radiant	Chemical
Mechanical	(Fluid) Mechanical & Acoustic Effects: eg. Diaphram, Gravity Balance	Friction Effects (eg. Friction Calorimeter)	Piezoelectricity Piezoresistivity Resistive, Capacitive, and Inductive Effects	Magnetochemical Effects: eg. Piezomagnetic Effect	Photoelastic systems (Stressed-induced Birefingence) Interferometers Doppler Effect	
Thermal	Thermal Expansion (Bimetalic strip) Radiometer Effect (Light Mill)		Seebeck Effect Thermoresistance Pyroelectricity Thermal (Johnson) Noise		Thermooptical Effects: eg, (in Liquid Crystal) Radiant Emission	Reaction Activation eg, Thermal Dissociation
Electrical	Electrokinetic & Electromechanical Effects: eg, Piezoelectricity Electrometer Ampere's Law	Joule (Resistive) Heating Peltier Effect	Charge Collectors Langmuir Probe	Biot-Savart's Law	Electrooptical Effects: eg, Kerr Effect Pockel Effect	Electrolysis Electromigration
Magnetic	Magnetomechanical Effects: eg, Magnetostriction Magnetometer	Thermomagnetic Effects: eg., Righi-Leudc Effects Galvanomagnetic Effects: eg, Ettingshauen Effects	Thermomagnetic Effects: eg. Ettingshusen-Nernst Effect Galvanometirc Effects: eg. Hall Effect		Magnetooptical Effects: eg, Faraday Effect Cotton-Mouton Effect	
Radiant	Radiation Pressure	Bolometer Thermopile	Photoelectric effects: eg. Photovoltaic Effect Photoconductive effect		Photoelectric Effects Optical Bistability	Photosynthesis, -dissociation
Chemical	Hygrometer Electrodeposition Cell Photoacoustic Effect	Calorimeter Thermal Conductivity	Potentiometry, Conductimetry, Amperometry, Flame Ionaisation, Gas Sensitive Field effect	Neuclear Magnetic Resonance	(Emission and Absorption) Spectroscopy Chemiluminescence	

Sensor World Market Forecast

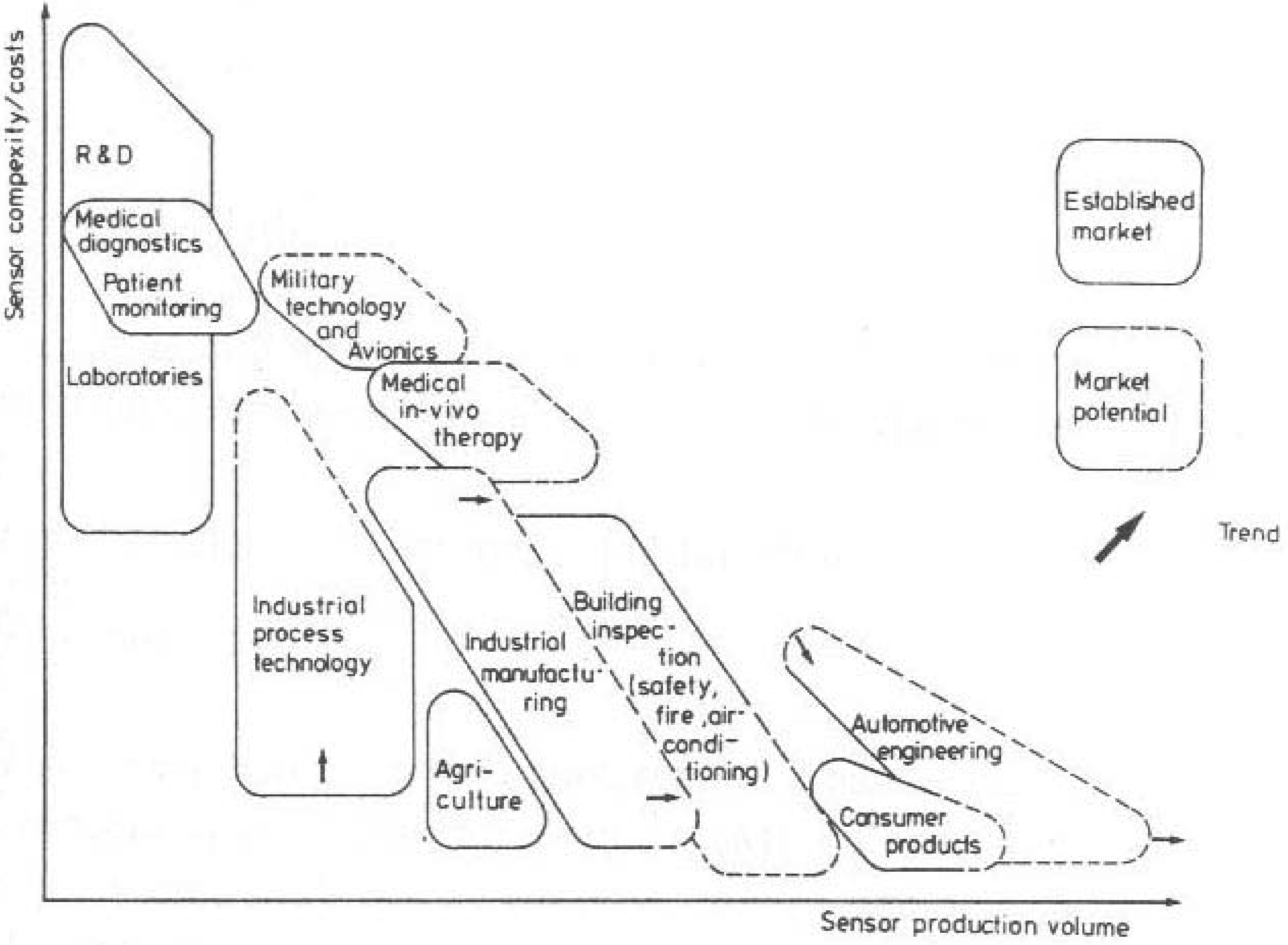
Sensor market categories:

- Machinery manufacturers and suppliers
- Processing industries
- Aerospace and shipbuilding
- Construction sector
- Consumer and electronics
- Automotive
- Others

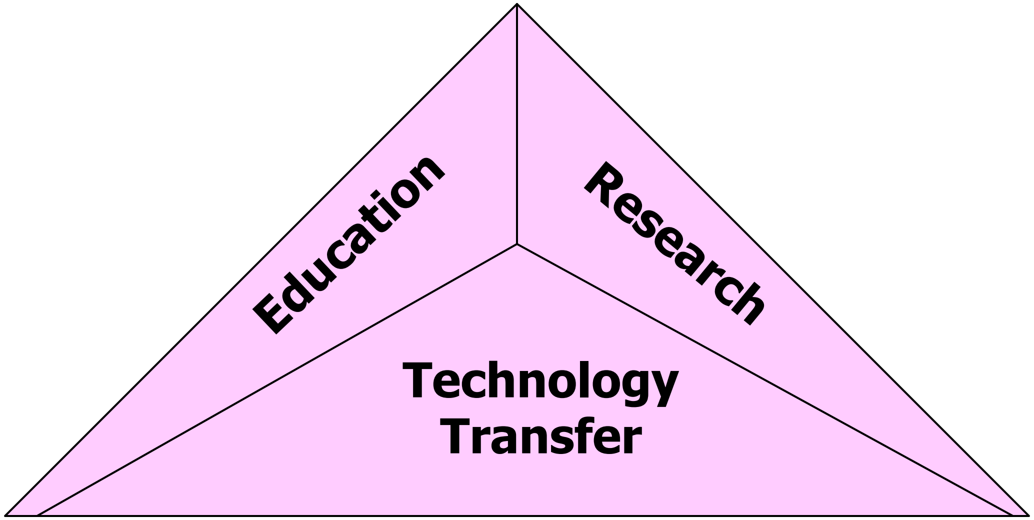
Projected in 2003	Overall sensor market: \$42.2 B Automotive: \$10.5 B (25%; 56 million cars/yr)
Projected by 2006	US demand in Chemical and Biosensors to reach \$2.7B
Now till 2010	Annual growth rate is projected to be 4-5%

Refs: 1. Industrial Sensor Technologies and Market, BCC Inc. Report, GB-200R, Jan. 2002.
2. Intechno Consulting Home Page: www.intechnoconsulting.com

Market Segments and Trends in Sensor Technology (log scale)



Center for industrial sensors and measurements (CISM)



Development of Harsh Environment Sensors

Combustion Gas Sensors

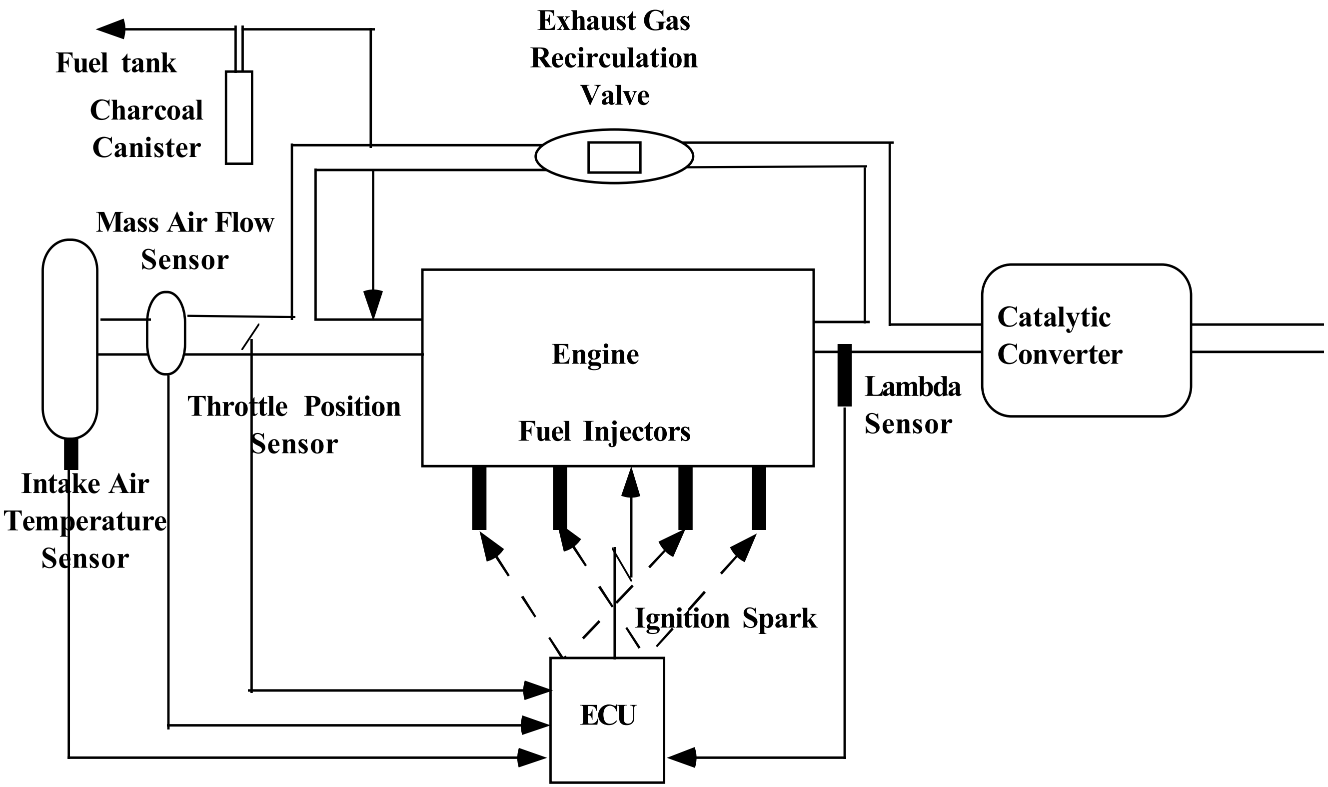
Specifications	CO	O_2	NO_x (total)	HC_s	CO_2
Applications	Domestic Aerospace Automotive Air quality Glass	Ceramic Kiln Utility, Glass Heat-treating Automotive Petroleum	Automotive Utility, Glass Aerospace Air quality Petroleum	Automotive Utility Aerospace Air quality	Automotive Domestic Food Corrosion Air quality
Temp. Range (°C)	RT - 1000	600 - 1400	200 - 1000	400 - 1000	25 - 800
Concentration Range	35 ppm - 5%	2 ppm – 21%	100-1000 ppm	1 ppm - 2%	400 ppm-10%
Sensitivity	10 - 1,000*	38.35 mV/dec***	38.35 – 153.4 mV/dec	2 – 100*	76.7 mV/dec
Response Time(ms)**	1000 - 10,000	< 1000	2000 - 20,000	10 - 1000	10 - 1000
Interference	≤1% to [_] ppm of H_2, H_2O, NO_X, C_2H_5OH, C_XH_Y	≤1% to [_] ppm of CO, C_XH_Y	≤5% to [_] ppm of CO, H_2, O_2, C_XH_Y	≤1% to [_] ppm of CO, H_2O, C_XH_Y	O_2, H_2O, NO_x
Poisoning	in SO_X, soots	soots	in SO_X, soots	SO_X, soots	SO_X, soots
Reproducibility (%)	< ± 2	< ± 2	≤ ± 2	< ± 2	< ± 2
Stability (%/year)	< 2	< 2	≤ ± 2	< 2	< 2
Lifetime-(min hrs)	45,000	100,000	50,000	100,000	50,000
Power Requirements	DC/battery	DC/battery	DC/battery	DC/battery	DC/battery

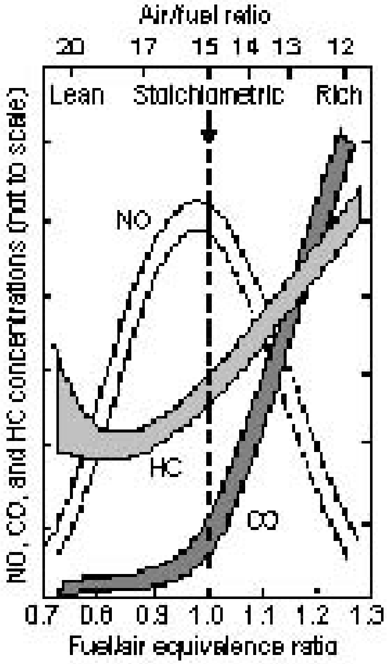
* Resistance normalized by resistance in the absence of the sensing gas.

** Response time defined as the time to achieve 90% of the final change in the sensor signal.

*** Nernst slope (RT/nF; 1<n<4; 38.35 mV/decade for n=4 and 153.4 mV/decade for n=1) at 500 C

INTERNAL ENGINE COMBUSTION EMISSIONS

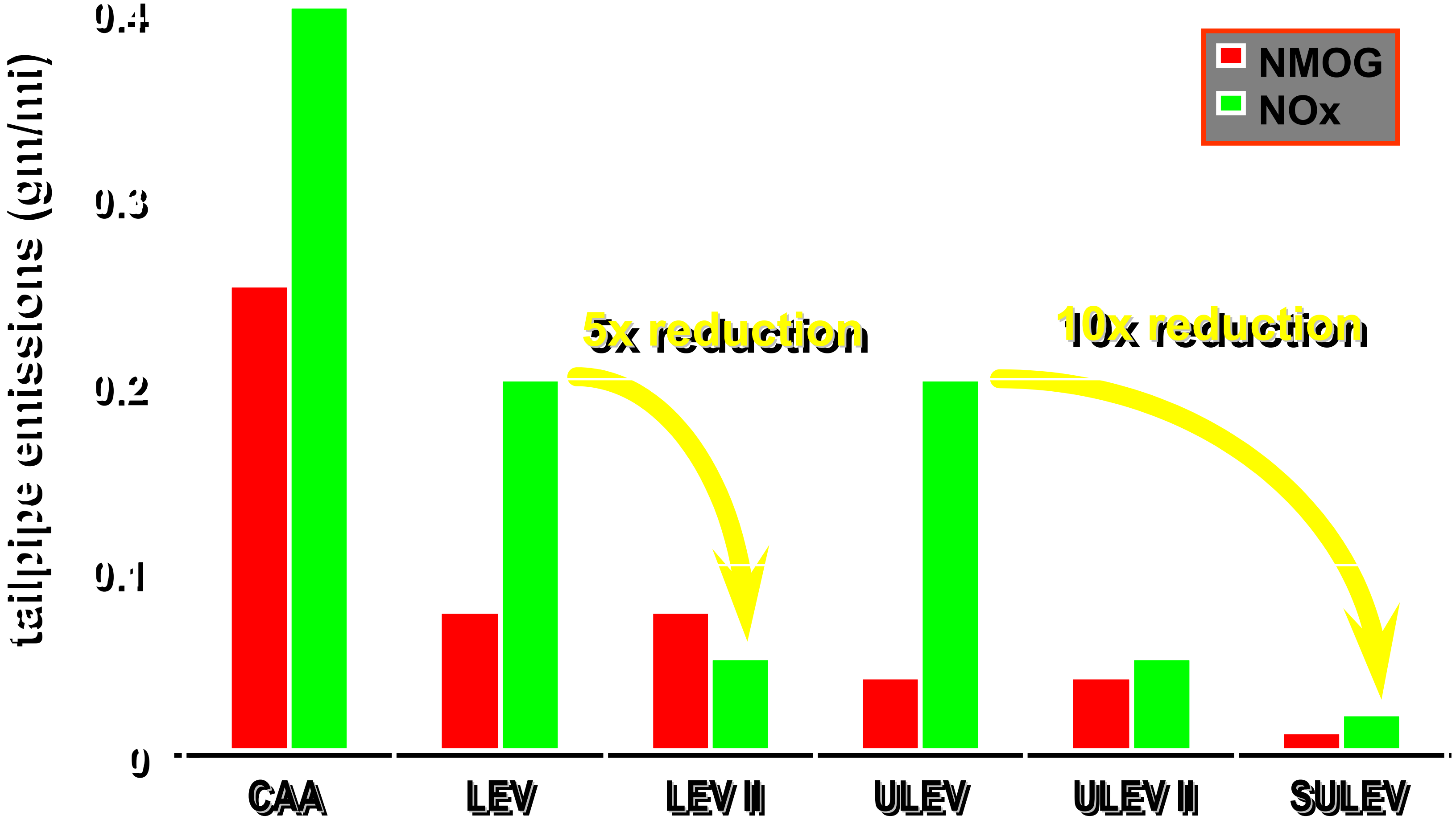




In last 60 years, from 40 million to 700 million vehicles and is projected to grow to 920 million by 2010.

California Emission Standards

Passenger Cars



Acknowledgement: Dr. G. Rizzoni, OSU

Sensor Needs in the Glass Industry

(Glass Industry: Technology Road Map, DOE, April 2002)

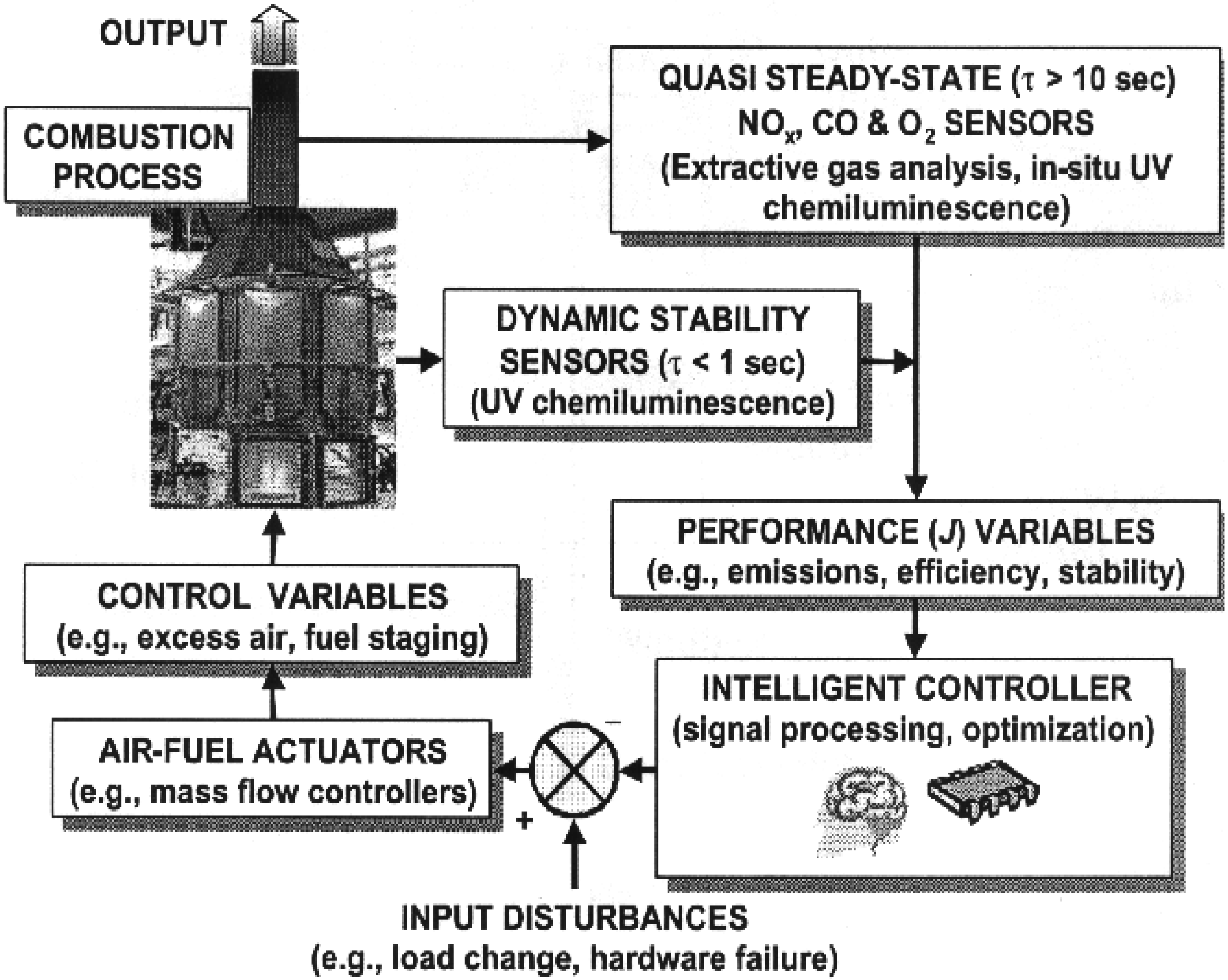
- Temperature monitoring in and above the melt (1350 – 1600 C)
  - Longer lasting sheathing material for thermocouples/durable ceramic thermistors
- Chemical sensors for polyvalent ion (S & Fe) in the melt
- Acoustic sensors for bubble defects and viscosity of the melt
- Flue gas (e.g., NO_x, CO and O_2) monitoring for burner control*
  - Monitoring within the hot-zone (500 – 1000 C) for burner feedback

    ⇒Need for high-temperature sensors

Needs in the metal processing industries are similar and challenging because of hostile environment

**Estimated energy use – 250 trillion Btu ⇒ Energy expenditures - $1.7 billion*
Source: US Dept. of Commerce & US Energy Info Admin.

Active Combustion Control of a Natural Gas-Burner



OUTPUT

COMBUSTION PROCESS

QUASI STEADY-STATE ($\tau > 10$ sec)
NO_x, CO & O_2 SENSORS
(Extractive gas analysis, in-situ UV chemiluminescence)

DYNAMIC STABILITY SENSORS ($\tau < 1$ sec)
(UV chemiluminescence)

PERFORMANCE (*J*) VARIABLES
(e.g., emissions, efficiency, stability)

INTELLIGENT CONTROLLER
(signal processing, optimization)

CONTROL VARIABLES
(e.g., excess air, fuel staging)

AIR-FUEL ACTUATORS
(e.g., mass flow controllers)

–

+

INPUT DISTURBANCES
(e.g., load change, hardware failure)

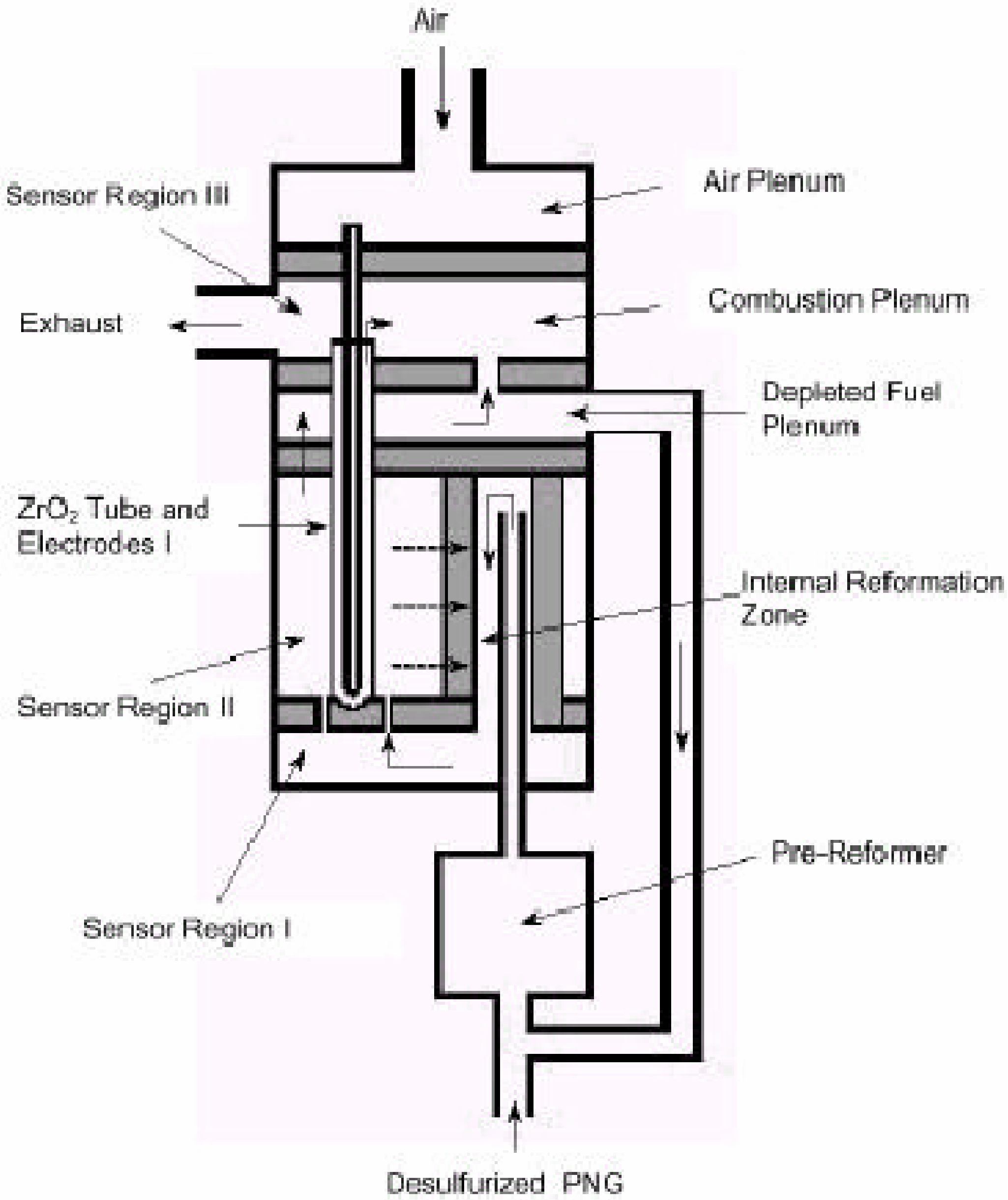
(Demayo, et al. 29th Symposium on Combustion, The Combustion Institute, 2002, in press)

Solid Oxide Fuel Cell (SOFC) Control

Region I: CO/H_2 and CH_4 sensors (efficiency of reforming process)

Region II: CO_2 sensor
(feedback for conversion of CO)

Region III: CO, H_2, O_2, CO_2 sensors (efficiency of total combustion)

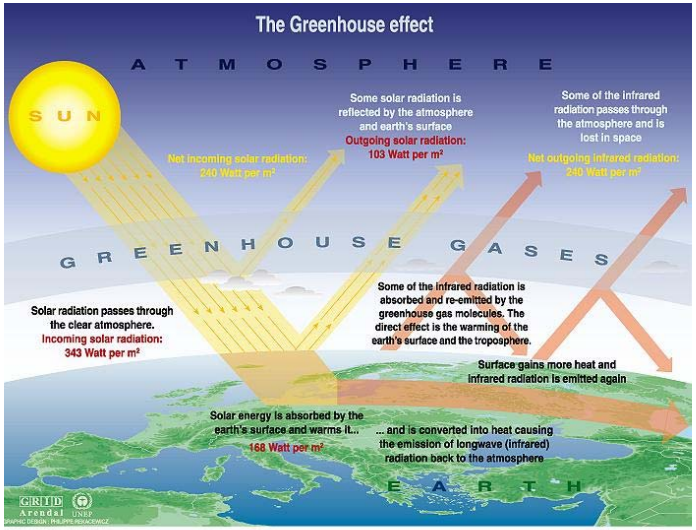


Chemical Sensor Needs *(Petroleum Industries)*

- **Upstream – *exploration and production***
  - Reservoir Analysis
    - H_2O analysis for cation (AAS) and anion ↑ pH sensor
  - Production Analysis
    - Gas composition by GC
  - Safety Monitoring – hydrocarbon (HC) by IR
  - Corrosion Monitoring – H_2S and CO_2
  - Environmental Monitoring – CO_2, NO_x
- **Downstream – *petroleum refining***
  - CO, NO_x, SO_x, hydrocarbons and particulates

Applications of CO_2 gas sensors

Environmental monitoring



Sources: Okanagan university college in Canada, Department of geography, University of Oxford, school of geography; United States Environmental Protection Agency (EPA), Washington; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge university press, 1996.

Biochemical properties of CO_2 gas

- Stimulating plant growth
- The indirect fertilization of plants
- Respiration rate control
- Controlling CO_2 component of MAP (modified atmospheric packaging)

Chemical properties of CO_2 gas

- Testing concrete carbonation
- CO_2 corrosion of steel in oil and gas industry

Decreasing Emissions Preserves Natural Beauty

Summary of our sensor work

(poster session and publications)

This Talk - Nano-structured ceramics

- platform for chemical sensing and catalysis
- inexpensive and highly scalable
- doesn’t need any patterning technology
- no need for highly trained technician

Why Nanostructured Ceramics?

- **Application of titania (TiO_2)**
  - Chemical sensing (resistive/semiconductive type)
  - Photo-catalysts and catalytic supports
    - Self-cleaning: tiles, windows, walls, signpost
    - Anti-bacterial: hospital, dishes
    - Environmental catalysis: air/water pollutants
    - Deodorizing: bathroom, kitchen
    - Photoinduced superhydrophilicity: antifog, contact lenses
    - Photocatalytic cancer treatment
  - Dye-sensitized solar cells

- World market for chemical sensors will grow to $12B by 2006

- For photo-catalysts, it will grow to $20B by 2005
(Mitsubishi research institute)

Fabrication techniques of nanomaterials

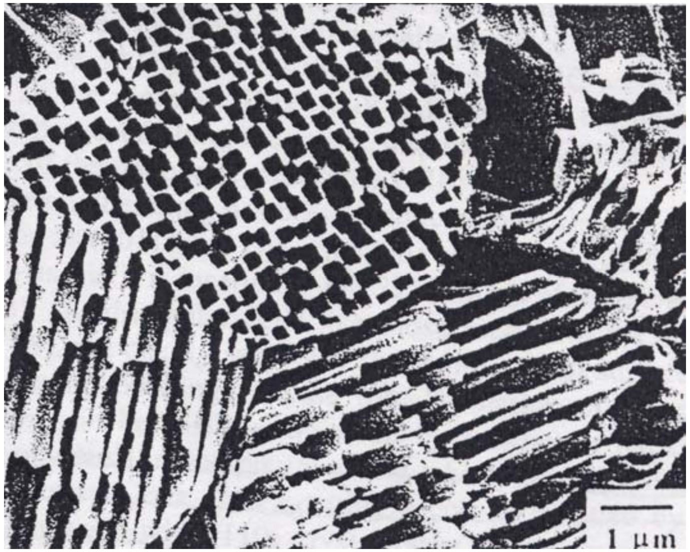
- Nanoparticles
  - Sol-gel
  - High energy ball milling
- Nanotube, nanowire, and nanobelt
  - Evaporation (Pan et al. Science 291 (2001) p1947)
  - Laser ablation (Alfredo et al. Science 279 (1998) p 208)
  - Anodization (Gong, Grimes et al. J. Mater. Res. 16 (2001) p 3331)
  - Electrospinning (Li et al. Nano lett. 3 (2003) p 555)
- Nanoporous structure
  - Emulsion templating (J. Mater. Res. 18 (2003) p 156)
  - Photoelectrochemical etching (Electrochem. Solid-State. Lett. 1 (1998) 175

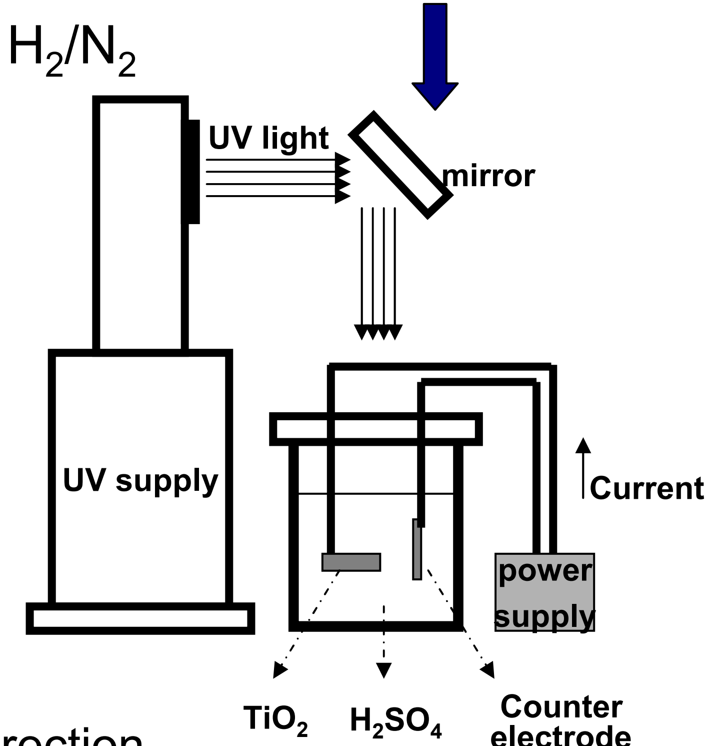
Photo-electrochemical (PEC) Etching

Sintering → H_2 heat treatment → PEC etching

1300 °C for 6hrs

700°C for 4hrs in 10% H_2/N_2





- The quadrangular holes are aligned in <001> direction
- The walls of the cells are {100}.
- Cell thickness is about 10-20 nm
- Length of the side of cells is 200-400 nm.

- Sugiura et al. Electrochem. Solid-State. Lett. 1 (1998) 175

Discovery of Titania Nanofibers

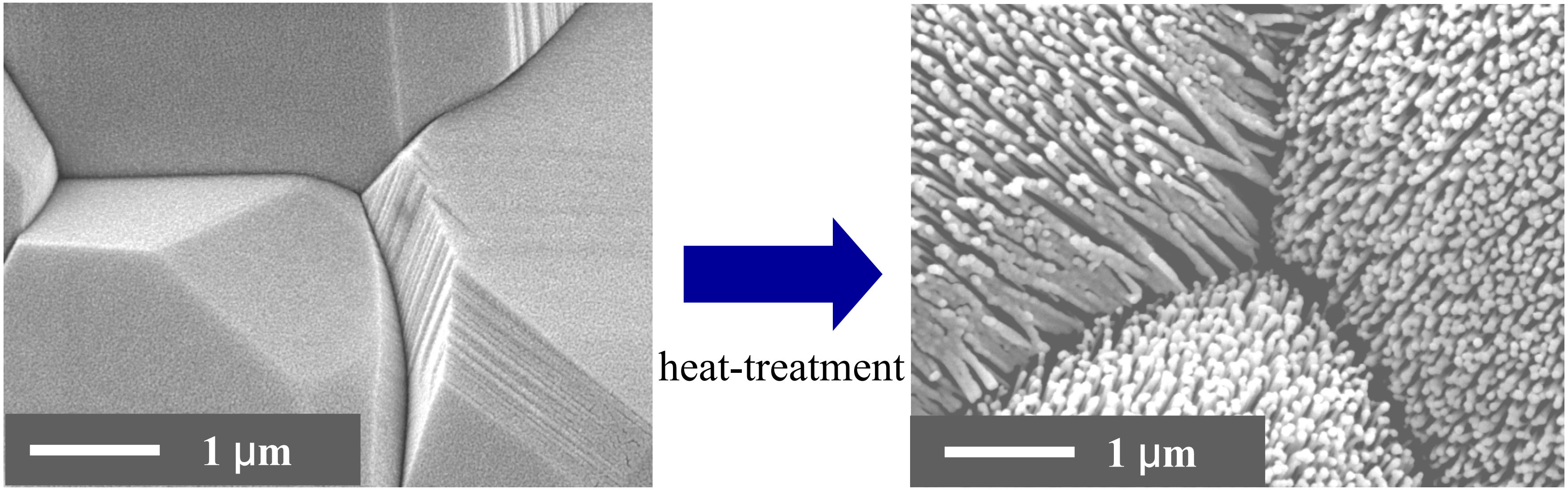
- Process

Adv. Matls., 16[3], 260 (2004)
Patent appl. 2003-678772

Sintering → H_2 heat treatment

1200 °C for 6hrs

700°C for 8hrs in 5% H_2/N_2



- Nano-fibers are parallel, oriented in the same direction
- Diameter of nano-fibers: 15 – 50 nm
  Length of nano-fibers: up to 5 μm

Questions to ponder …

- **How does this happen and how do we control it?**
- **Are the nano-fibers stable?**

  (stable in air up to 550 C)
- **Is this unique to TiO_2 or can other oxides exhibit this?**

  (initial indication in SnO_2)
- **Are they useful for any applications?**

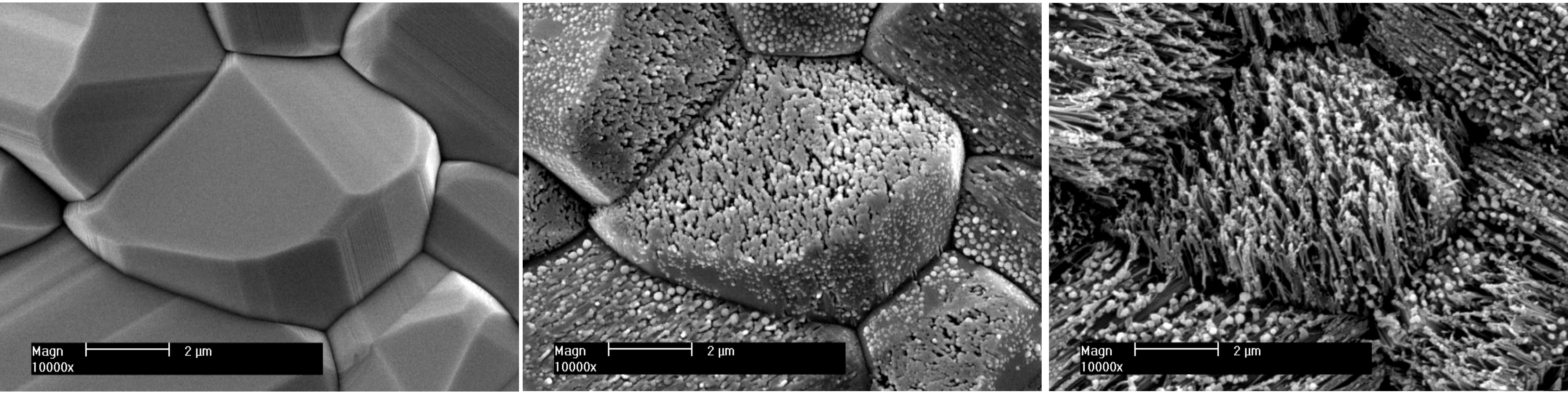
  (good H_2 sensing)
- **Is this a new avenue for micro- and nano-machining of ceramics?**

Only partial answers are known

What do we know?

Etching process creating fibers on the surface

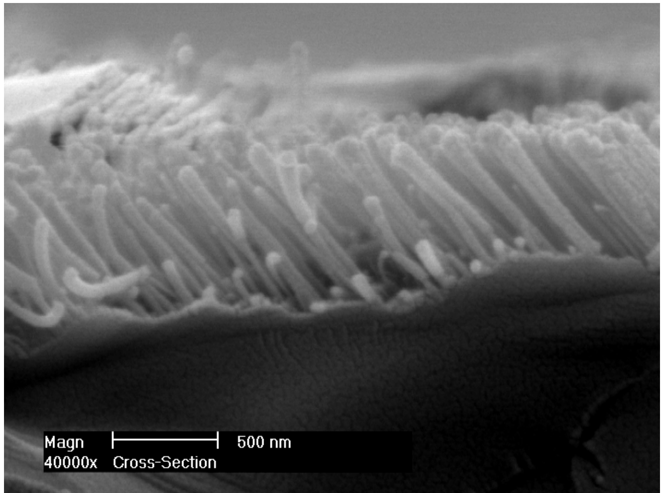
- Microstructure evolution during H_2/N_2 heat-treatment



t = 0

t = 10 min

t = 8 hrs

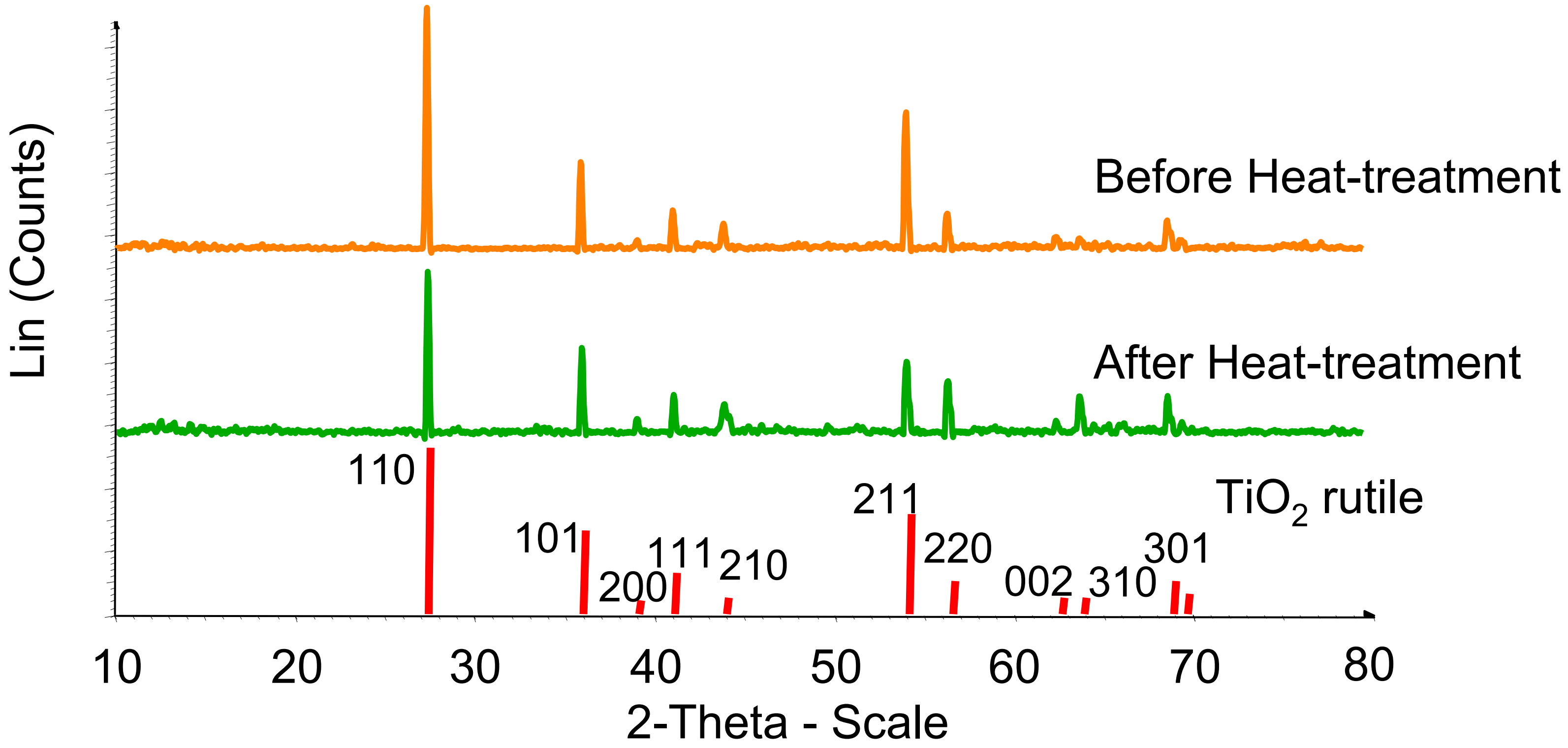


Fibers are formed by surface reaction

Exact reactions and reaction products are unknown

Phase of nanofibers?

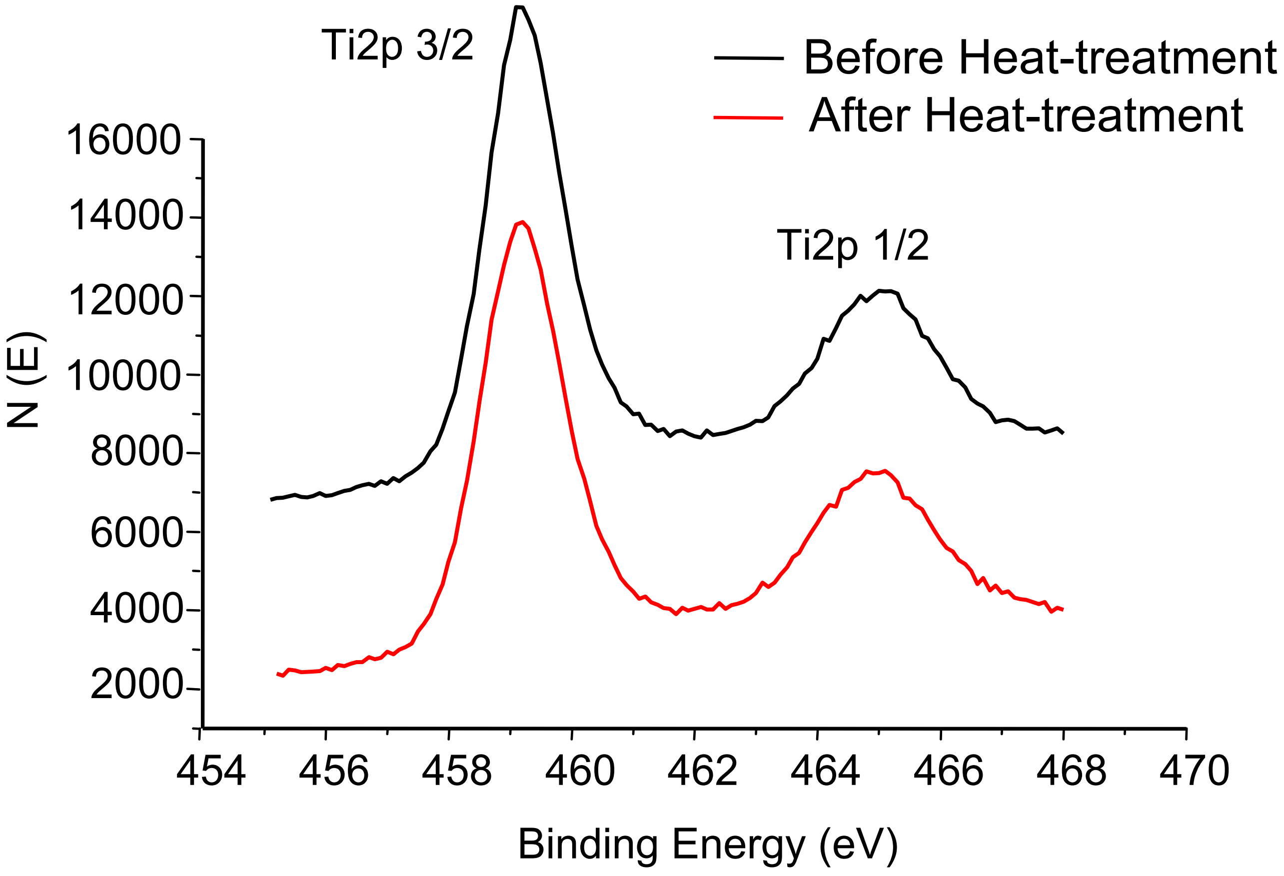
- XRD observation



- X-ray penetration depth is about 2 μm; XRD data include information on nano-fibers.
- Both phases are rutile.

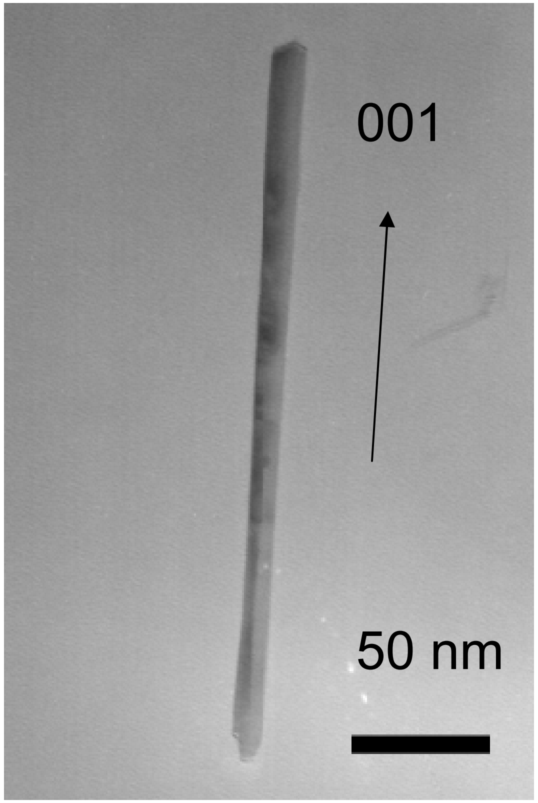
Any difference by XPS?

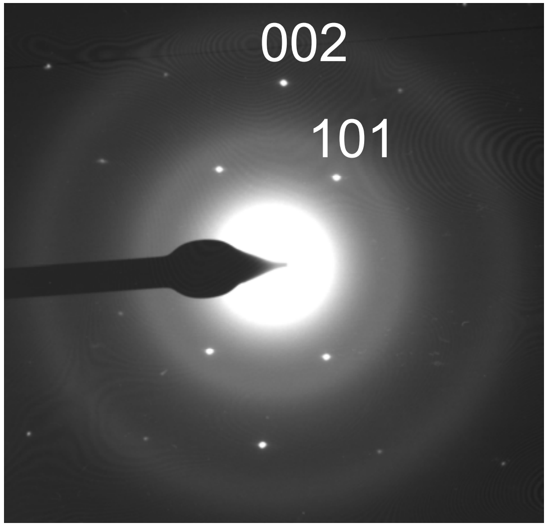
- XPS observation shows no difference in Ti oxidation state



Phase and fiber direction by TEM

- XRD and XPS confirms rutile TiO_2
- SAED confirms nano-fiber to be rutile TiO_2
- Fiber direction is (001) and it is single crystal

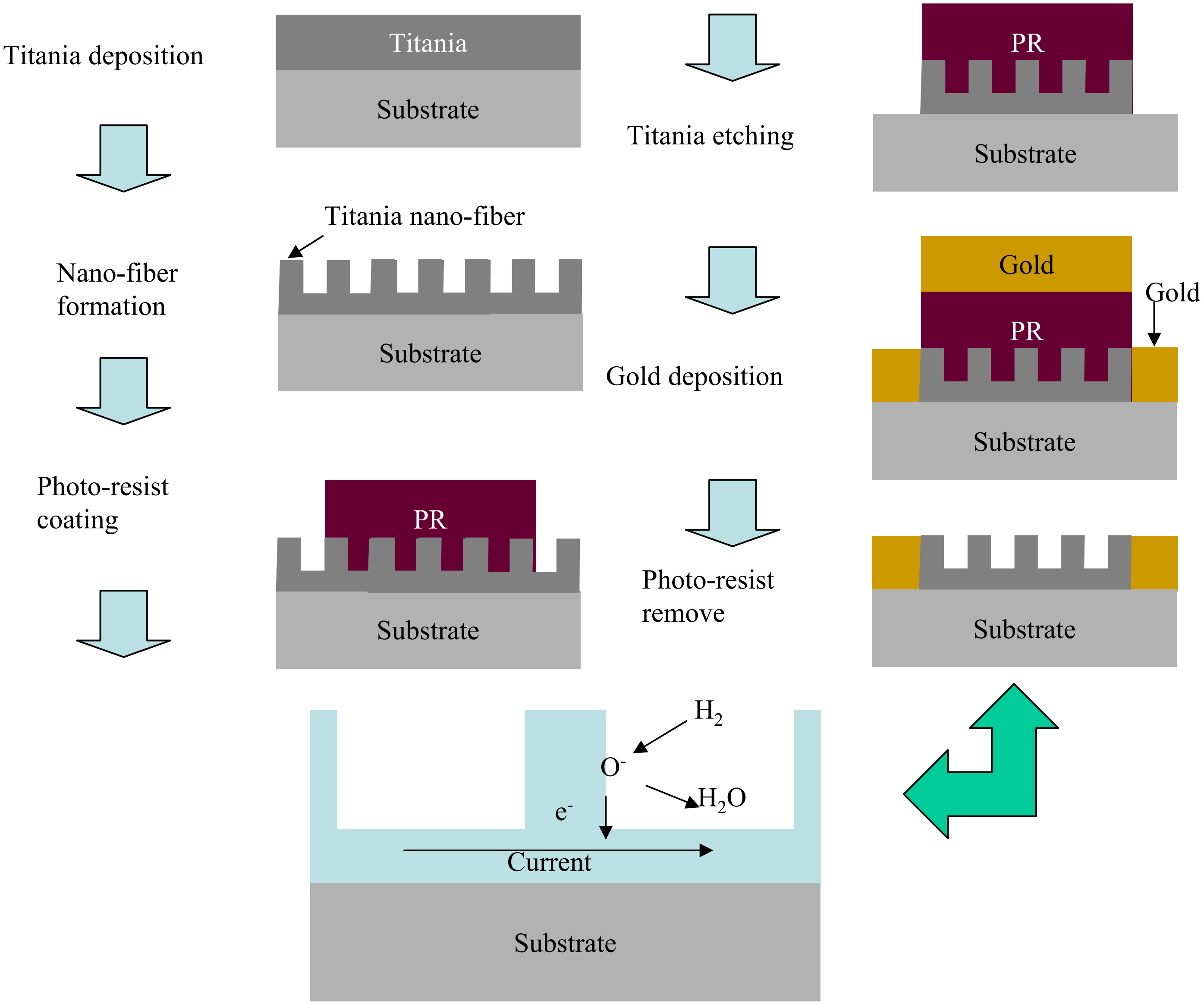




Why is the etching process anisotropic and selective?

Useful for any applications?

Measurements of electrical/chemical sensing property



Titania deposition

Nano-fiber formation

Photo-resist coating

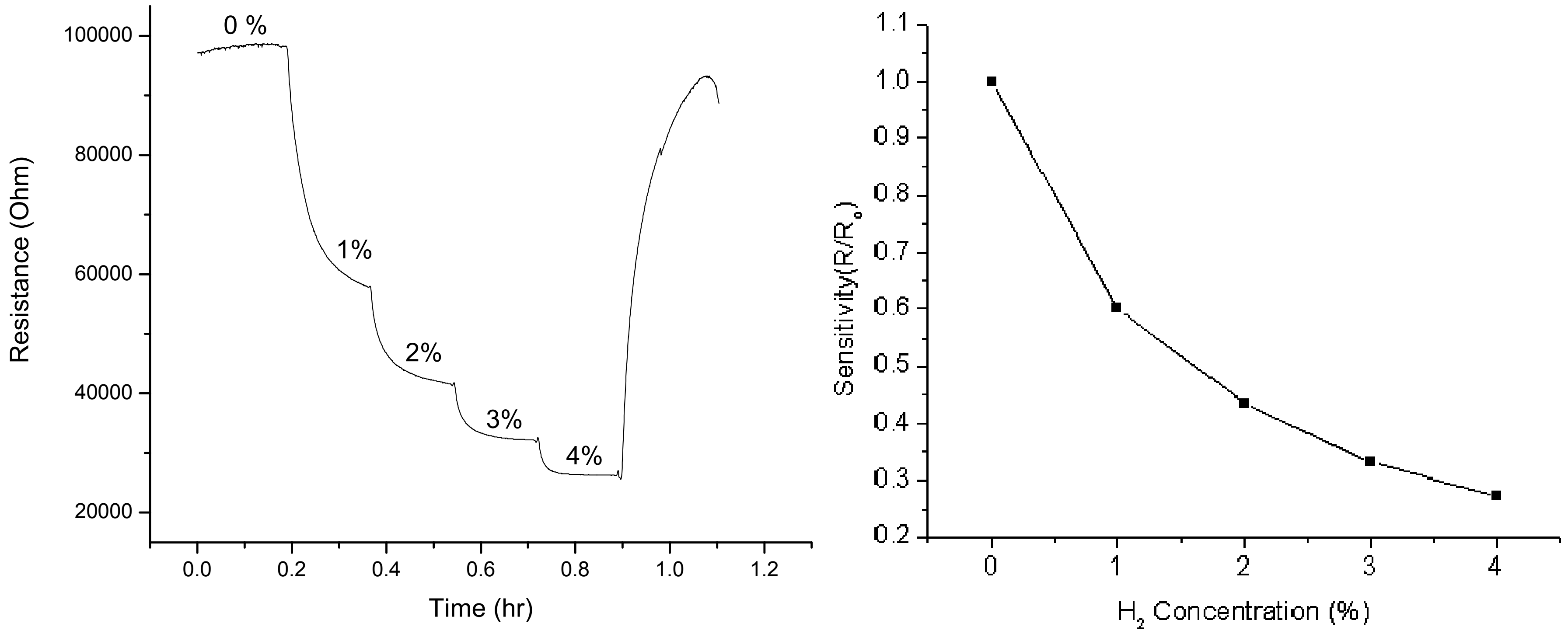
Titania etching

Gold deposition

Photo-resist remove

Preliminary sensing test for nano-fibers

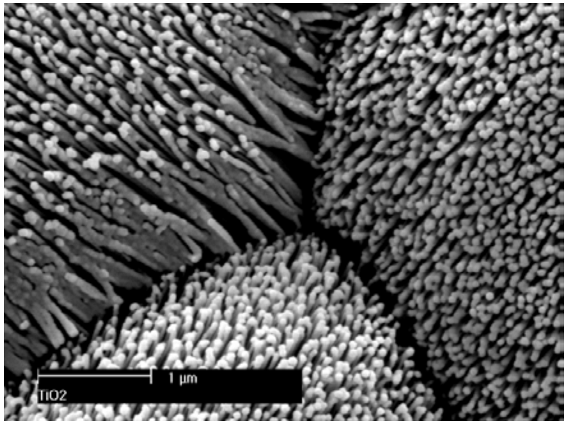
H_2 Sensing test at 400 °C



- Sensing characteristics are yet to be optimized
- Photo-catalytic activity needs to be explored

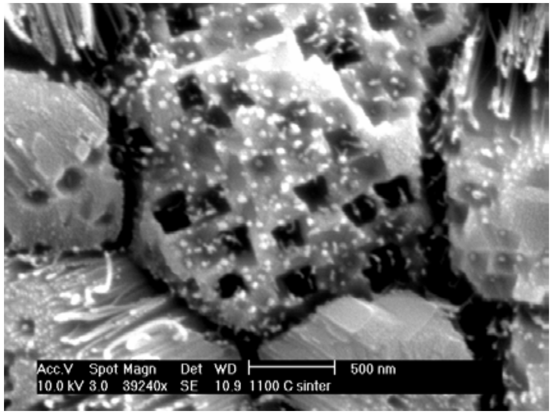
Ceramic Nano-machining?

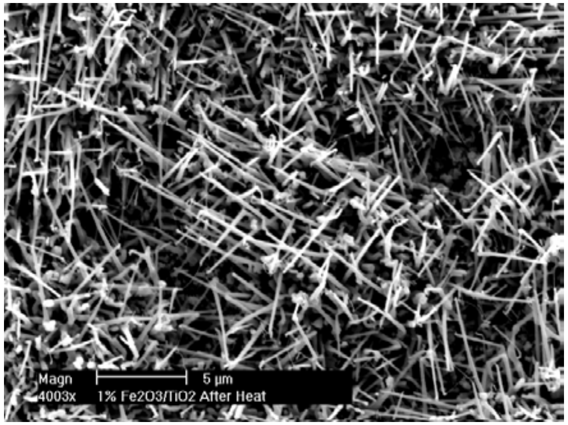
Wide variety of possibilities by gas-phase reaction



Nano-fibers

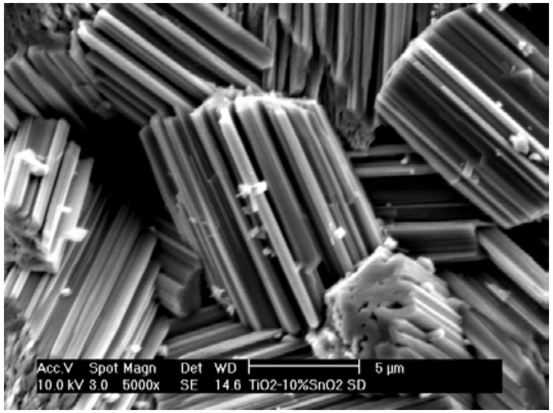
Nano-channels





Nano-whiskers

Nano-lamellar



In the media …

“Tiny nano-fingers to support sensors and other applications”

OSU Research News (December, 2003)
Eurekalert.org (December, 2003)
Innovations-report.com (December, 2003)
Nanoxchange.com (December, 2003)
Jef’s web files (December, 2003)
The Hindu (India, December, 2003)
Newswise (January, 2004)
Ceramic Bulletin (March and August 2004)

“Ceramic nano-fingers make cheap sensors”

Betterhumans.com (January, 2004)

“Nano-fingers for the future”

Sensors (January, 2004)

“New sensor from nano-fingers”

e4engineering.com (January, 2004)

“Chemically carved ceramics pave way for better environmental sensors”

Frost & Sullivan (January, 2004)

“Nano-fingers with environmental security implications”

Environmental Security Scanning (December, 2003)

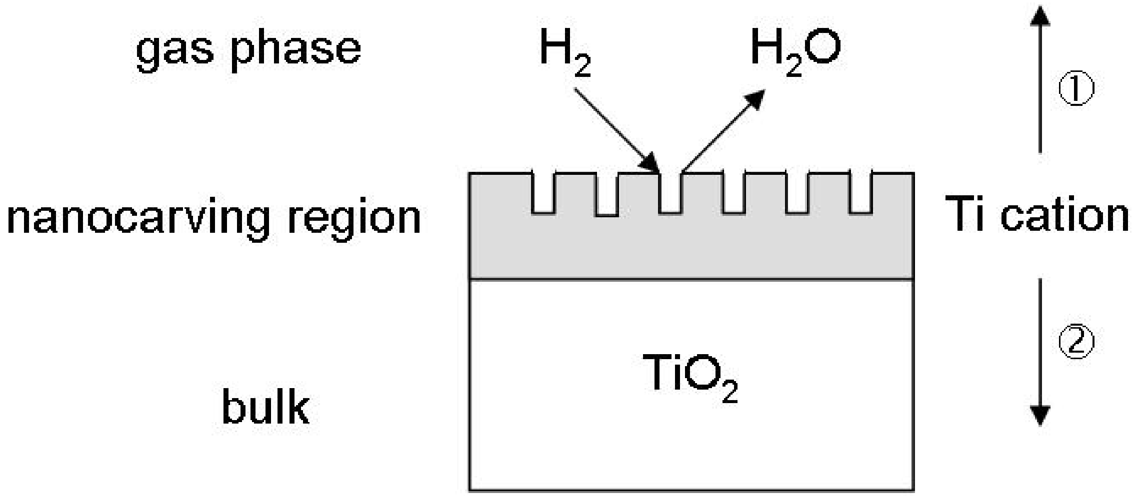
Challenge …..

"How does this happen?
Nobody knows.
Yoo hopes to earn his PhD figuring it out."

Business Week (January 19, 2004)

Mechanism and Selectivity of Etching

$$TiO_2 + H_2(g) = TiO_{2-x} + H_2O(g)$$



gas phase

H_2

H_2O

①

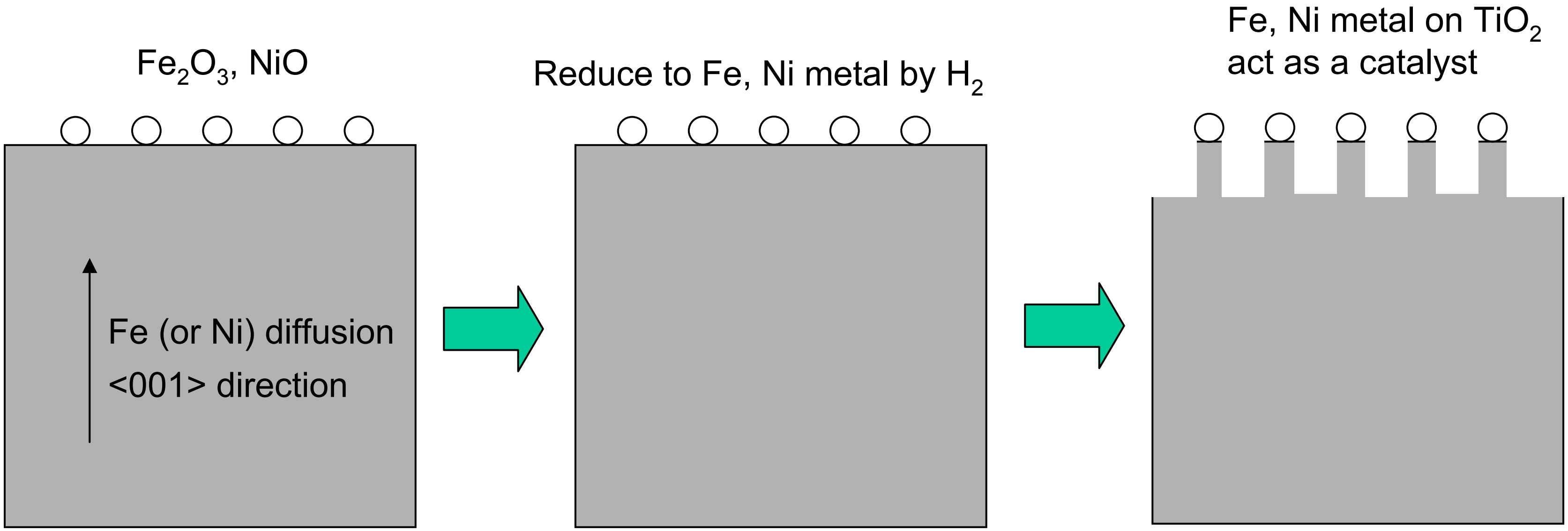
nanocarving region

Ti cation

bulk

TiO_2

②



Fe_2O_3, NiO

Fe (or Ni) diffusion

<001> direction

Reduce to Fe, Ni metal by H_2

Fe, Ni metal on TiO_2

act as a catalyst

General Challenges and Opportunities for Ceramic-based Sensors

Stability (in hostile environment)
- Materials R&D

Sensitivity
- Nano-materials/structures

Selectivity
- Catalysts, membranes, sensor arrays

Response time
- Sub-/micro-seconds; thin film

Basic studies
- Mechanism, modeling and simulation of arrays

Manufacturing and miniaturization
- Micro-/nano-machining, packaging

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G. Hunter (NASA)

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